

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>G03F 7/029, 7/00</b>		<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 99/44099</b> <b>(43) International Publication Date:</b> 2 September 1999 (02.09.99)
<b>(21) International Application Number:</b> PCT/US99/04131 <b>(22) International Filing Date:</b> 25 February 1999 (25.02.99) <b>(30) Priority Data:</b> 60/075,892 25 February 1998 (25.02.98) US <b>(71) Applicant:</b> CYCOLOR, INC. [US/US]; 3385 Newmark Drive, Miamisburg, OH 45342 (US). <b>(72) Inventors:</b> POLYCARPOV, Alex; 971 Locust Court, Mason, OH 45040 (US). CAMILLUS, Joseph, C.; 2698 Wood Bluff, Dayton, OH 45458 (US). <b>(74) Agents:</b> LEVY, Mark, P. et al.; Thompson Hine & Flory LLP, 2000 Courthouse Plaza N.E., P.O. Box 8801, Dayton, OH 45401-8801 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
<b>(54) Title:</b> IMAGING SYSTEM EMPLOYING ENCAPSULATED RADIATION SENSITIVE COMPOSITION			
<b>(57) Abstract</b> <p>A photosensitive material comprising a support having a layer of microcapsules on one surface thereof, the microcapsules having an image-forming agent associated therewith and containing an internal phase including a photohardenable composition, the composition comprising a free radical addition polymerizable or crosslinkable compound and complex of an infrared sensitive cationic dye and a boranyl anion being capable of absorbing infrared radiation and producing free radicals which initiate free radical polymerization or crosslinking of the polymerizable or crosslinkable compound.</p>			

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

## **IMAGING SYSTEM EMPLOYING ENCAPSULATED RADIATION SENSITIVE COMPOSITION**

### **CROSS-REFERENCE TO RELATED APPLICATIONS**

The present invention claims priority under 35 U.S.C. §119 from Provisional Patent Application Serial No. 60/075,892, filed February 25, 1998.

### **BACKGROUND OF THE INVENTION**

This application is directed to an improvement in the imaging system which is described in U.S. Patents 4,399,209, 4,440,846 and 4,772,530 to Cycolor, Inc. These imaging systems employ a layer of photosensitive microcapsules. The microcapsules are prepared by microencapsulating a free radical polymerizable composition which contains an electron donating color precursor. Typically the image system assumes two forms. In one, the imaging system is a transfer system in which a support carrying a layer of photosensitive microcapsules is image-wise exposed to radiation and assembled with a developer sheet, e.g., a sheet containing a layer of a Lewis acid such as a phenolic resin. The assembly is subjected to pressure to rupture the microcapsules and the microcapsules image-wise leak their contents to the developer sheet where the color precursor is colored. In another embodiment, the imaging system is a self-contained imaging system in which the photosensitive microcapsules and the Lewis acid are carried on the surface of a common substrate in one layer or in juxtaposed layers. In a further embodiment of the invention, as described in U.S. Application Serial No. 08/570,658 and published International Application WO 95/34845, a layer containing photosensitive microcapsules and a developer material is interposed between two plastic films, at least one of which is transparent. Using a combination of an adhesive and a subbing layer, the films are permanently sealed to provide a film unit. This construction is advantageous because it prevents the chemical reactants in the imaging system from coming into contact with the user.

The imaging system is preferably a full color imaging system in which three different sets of microcapsules are used in combination and each set of microcapsules is

sensitive to a distinct wavelength band. This full color system is described in U.S. Patent 4,842,976. In accordance with one commercial manifestation of the imaging system, three sets of microcapsules respectively containing cyan, magenta and yellow color precursors are respectively sensitive to red, green and blue light are employed. In a further embodiment, these microcapsules are sensitized using a so-called "dye-borate photoinitiator" of the type described in U.S. Patent 4,772,530 to Gottschalk. These photoinitiators, in one embodiment, are complexes of cationic cyanine dyes and a boranyl anion such as a triphenylbutylboranyl anion. For making photocopies and other applications employing visible light sources, imaging systems employing red-sensitive, blue-sensitive and green-sensitive microcapsules are desirable but one of the difficulties that is encountered in designing an imaging system with red, green and blue sensitivity is cross-talk. That is, the absorption spectra of the red and/or green and/or blue photoinitiators may overlap. In this case, it is important that in exposing the microcapsule to limit the amount of light which occurs in an overlapping region. Otherwise, the color quality of the reproduction will not be good. The art discloses a number of approaches that can be taken to mitigate this problem. However, with the proliferation of digital imaging systems, there are a host of applications in which red, green and blue sensitivity is not required. In particular printers can be designed which employ radiation sources which emit at wavelengths outside the visible spectrum, for example, in the infrared region. This presents an opportunity to minimize the problems associated with cross-talk since it is no longer necessary to restrict the sensitivity range of a photosensitive material to the visible region, the sensitivity of the imaging system can be extended into the infrared region at one end of the spectrum and optionally the ultraviolet region at the other end.

## SUMMARY OF THE INVENTION

In accordance with the present invention, the foregoing imaging system and, more particularly, the imaging system described in U.S. Patent 4,772,530, is modified to include one or more infrared photosensitive compositions and, more particularly, to include one or more photosensitive compositions in which the photoinitiator is a complex between an infrared-sensitive dye and a boranyl anion of the type mentioned above.

Accordingly, one embodiment of the invention resides in an imaging system comprising a support having a layer of at least one set of photosensitive microcapsules on the surface thereof, said microcapsules being sensitive to distinct band of radiation and containing a complex of an infrared sensitive cationic dye and a boranyl anion.

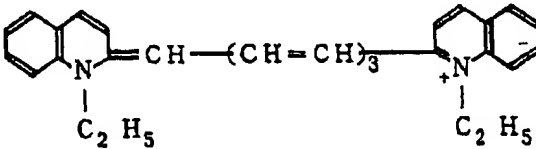
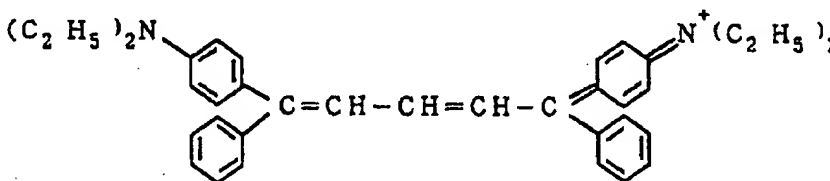
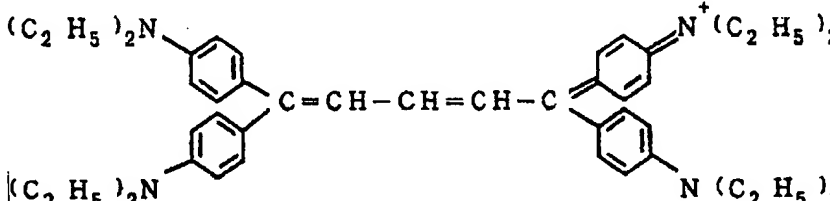
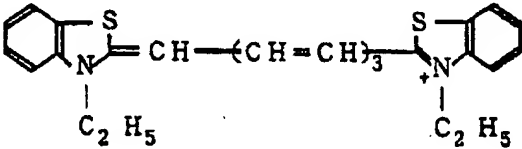
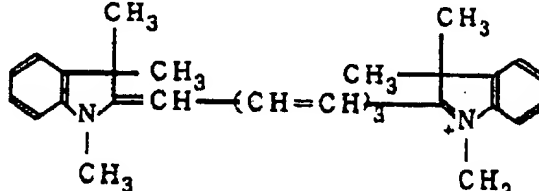
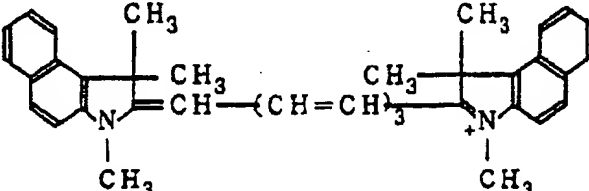
In another embodiment, the imaging system includes cyan forming, magenta forming and yellow forming capsules and at least one set of capsules includes an infrared sensitive dye borate compound as a photoinitiator. Optionally at least one other set includes a visible light sensitive dye borate compound or an ultraviolet initiator.

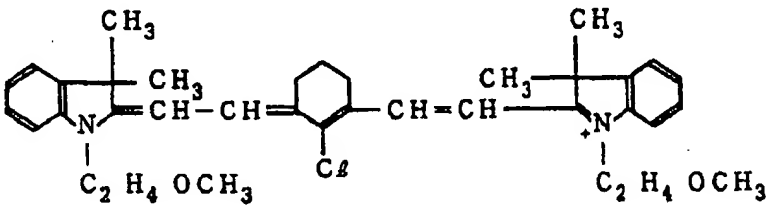
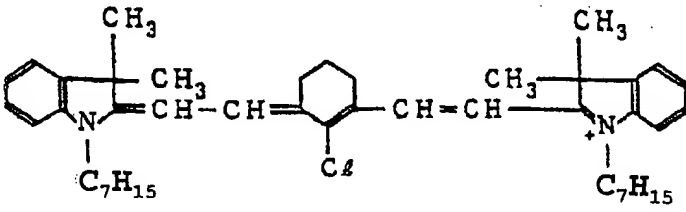
In still another embodiment, all three sets of microcapsules contain a photohardenable composition containing a complex of a cationic infrared sensitive dye and a boranyl anion.

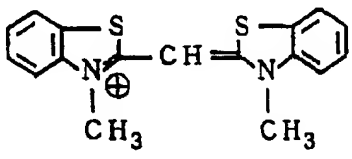
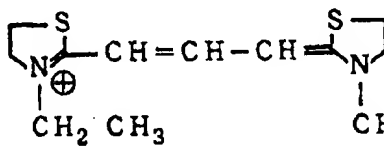
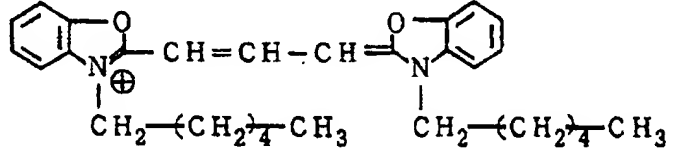
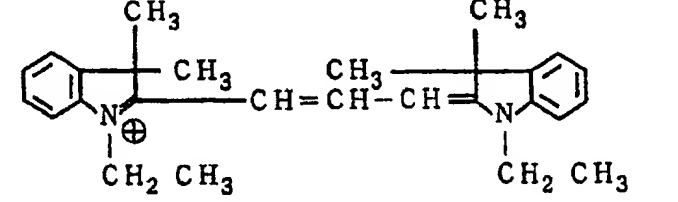
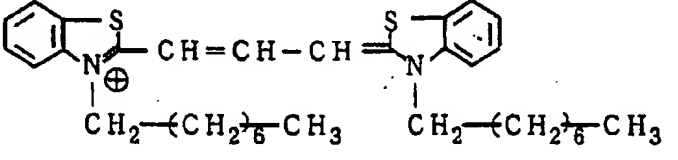
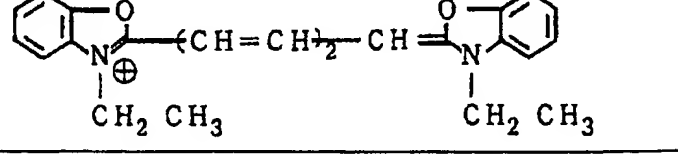
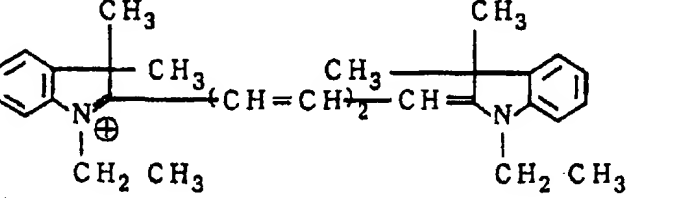
## DETAILED DESCRIPTION OF THE INVENTION

Examples of infrared-sensitive photoinitiators which can be employed in the imaging system of the present invention are described in Japanese Published Applications 3-221506; 4-261405; 8-100011; 8-100012; and 8-34808, all of which are incorporated herein by reference for a description of the cationic dyes and methods for obtaining the photoinitiators. A table of the infrared sensitive cationic dyes described in the aforementioned patents is provided in the following Table 1 where "Ph" indicates a phenyl group:

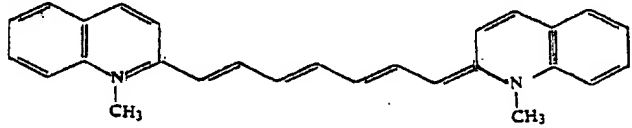
Table 1

No.	Dye	$\lambda_{\text{max}}$ (TMPT)
1		820nm
2		830nm
3		822nm
4		768nm
5		748nm
6		785nm

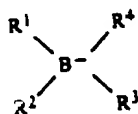
No.	Dye -	$\lambda_{\text{max}}$ (TMPT)
7		787nm
7A		813nm

No.	Dye	$\lambda_{\max}$ (CHCl <sub>3</sub> )
8		428nm
9		450nm
10		492nm
11		550nm
12		568nm
13		590nm
14		640nm



No.	Dye	
15		814nm

The infrared dyes in Table 1 are complexed with a borate anion. Any of the borate anions described in U.S. Patent 4,772,530 can be used in this invention. The preferred boranyl anion is a triphenyl n-butylboranyl anion. The anions can be represented by the general formula (I):



where  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ , and  $\text{R}^4$  are independently selected from the group consisting of alkyl, aryl, alkaryl, allyl, aralkyl, alkenyl, alkynyl, alicyclic and saturated or unsaturated heterocyclic groups.

For example particularly preferred anions are triphenylalkylborate and trianisylalkylborate anions such as triphenylbutylborate and trianisylbutylborate anions because they readily dissociate to triphenylborane or trianisylborane and a butyl radical. On the other hand tetrabutylborate anion does not work well presumably because the tetrabutylborate radical is not stable and it readily accepts an electron back from the dye in a back electron transfer and does not dissociate efficiently. Likewise, tetraphenylborate anion is very poor because the phenyl radical is not easily formed.

Preferably, at least one but not more than three of  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  is an alkyl group. Each of  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  is an alkyl group. Each of  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  can contain up to 20 carbon atoms, and they typically contain 1 to 7 carbon atoms. More preferably  $R^1$ - $R^4$  are a combination of alkyl group(s) and aryl group(s) or aralkyl group(s) and still more preferably a combination of three aryl groups and one alkyl group.

Representative examples of alkyl groups represented by  $R^1$ - $R^4$  are methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, stearyl, etc. and can be straight or branched chain and possibly cyclic. The alkyl groups may be substituted, for example, by one or more halogen, cyano, acyloxy, acyl, aryl, alkoxy or hydroxy groups.

Representative examples of aryl groups represented by  $R^1$ - $R^4$  include phenyl, naphthyl and substituted aryl groups such as anisyl. Alkaryl groups include methylphenyl, dimethylphenyl, etc. Representative examples of aralkyl groups represented by groups include benzyl. Representative alicyclic groups include cyclobutyl, cyclopentyl, and cyclohexyl groups. Examples of an alkynyl group are propynyl and ethynyl, and examples of alkenyl groups include a vinyl group.

Other infrared sensitive complexes useful as photoinitiators in the invention described in Japanese Application 4-261405 are shown in Table 2:

Table 2

(A)

		Ar	R
19A 19B 19C	$\left[ \begin{array}{c} (\text{CH}_3\text{CH}_2)_2\text{N}-\text{C}_6\text{H}_4-\text{N}=\text{C}_{10}\text{H}_6\text{O} \\ \text{Ni} \end{array} \right]_2^{2+} \left[ \begin{array}{c} \text{Ar} \\   \\ \text{Ar}-\text{B}-\text{R} \\   \\ \text{Ar} \end{array} \right]_2^-$	phenyl anisyl phenyl	n-butyl n-hexyl n-octyl
20A 20B 20C	$\left[ \begin{array}{c} (\text{CH}_3\text{CH}_2)_2\text{N}-\text{C}_6\text{H}_4-\text{N}=\text{C}_{10}\text{H}_6\text{O} \\ \text{Cu} \end{array} \right]_2^{2+} \left[ \begin{array}{c} \text{Ar} \\   \\ \text{Ar}-\text{B}-\text{R} \\   \\ \text{Ar} \end{array} \right]_2^-$	phenyl anisyl phenyl	n-butyl n-hexyl n-octyl
21A 21B 21C	$\left[ \begin{array}{c} (\text{CH}_3\text{CH}_2)_2\text{N}-\text{C}_6\text{H}_4-\text{N}=\text{C}_{10}\text{H}_6\text{O} \\ \text{Ni} \end{array} \right]_3^{2+} \left[ \begin{array}{c} \text{Ar} \\   \\ \text{Ar}-\text{B}-\text{R} \\   \\ \text{Ar} \end{array} \right]_2^-$	phenyl anisyl phenyl	n-butyl n-hexyl n-octyl

(B)

		Ar	R
22A 22B 22C	$\left[ \begin{array}{c} (\text{CH}_3\text{CH}_2)_2\text{N}-\text{C}_6\text{H}_4-\text{N}=\text{C}_{10}\text{H}_6\text{O} \\ \text{Cu} \end{array} \right]_3^{2+} \left[ \begin{array}{c} \text{Ar} \\   \\ \text{Ar}-\text{B}-\text{R} \\   \\ \text{Ar} \end{array} \right]_2^-$	phenyl anisyl phenyl	n-butyl n-hexyl n-octyl
23	$\left[ \begin{array}{c} (\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{N}-\text{C}_6\text{H}_4-\text{N}=\text{C}_{10}\text{H}_6\text{O} \\ \text{Ni} \end{array} \right]_2^{2+} \left[ \begin{array}{c} \text{Ph} \\   \\ \text{Ph}-\text{B}-\text{Bu} \\   \\ \text{Ph} \end{array} \right]_2^-$		
24	$\left[ \begin{array}{c} (\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{N}-\text{C}_6\text{H}_4-\text{N}=\text{C}_{10}\text{H}_6\text{O} \\ \text{Cu} \end{array} \right]_2^{2+} \left[ \begin{array}{c} \text{Ph} \\   \\ \text{Ph}-\text{B}-\text{Bu} \\   \\ \text{Ph} \end{array} \right]_2^-$		

(C)

		Ar	R
25	$\left[ \begin{array}{c} \text{NCC}_2\text{H}_4 \\   \\ \text{N} - \text{C}_6\text{H}_4 - \text{N} = \text{C}_{10}\text{H}_6\text{O} \\   \\ \text{NCC}_2\text{H}_4 \end{array} \right]_2^{2+} \left[ \begin{array}{c} \text{Ph} \\   \\ \text{Ph}-\text{B}-\text{Bu} \\   \\ \text{Ph} \end{array} \right]_2^-$		
26	$\left[ \begin{array}{c} \text{CH}_3\text{CH}_2 \\   \\ \text{N} - \text{C}_6\text{H}_4 - \text{N} = \text{C}_{10}\text{H}_6\text{O} \\   \\ \text{NCC}_2\text{H}_4 \end{array} \right]_2^{2+} \left[ \begin{array}{c} \text{Ph} \\   \\ \text{Ph}-\text{B}-\text{Bu} \\   \\ \text{Ph} \end{array} \right]_2^-$		

(D)

		Ar	R
27A 27B 27C	$\left[ \begin{array}{c} (\text{CH}_3\text{OCC}_2\text{H}_4)_2\text{N} - \text{C}_6\text{H}_3(\text{Cl}) - \text{N} = \text{C}_{10}\text{H}_6\text{O} \\   \\ \text{N} \end{array} \right]_2^{2+} \left[ \begin{array}{c} \text{Ar} \\   \\ \text{Ar}-\text{B}-\text{R} \\   \\ \text{Ar} \end{array} \right]_2^-$	phenyl anisyl phenyl	n-butyl n-hexyl n-octyl
28A 28B 28C	$\left[ \begin{array}{c} (\text{CH}_3\text{OCC}_2\text{H}_4)_2\text{N} - \text{C}_6\text{H}_3(\text{Cl}) - \text{N} = \text{C}_{10}\text{H}_6\text{O} \\   \\ \text{Cu} \end{array} \right]_2^{2+} \left[ \begin{array}{c} \text{Ar} \\   \\ \text{Ar}-\text{B}-\text{R} \\   \\ \text{Ar} \end{array} \right]_2^-$	phenyl anisyl phenyl	n-butyl n-hexyl n-octyl
29A 29B 29C	$\left[ \begin{array}{c} (\text{CH}_3\text{OC}_2\text{H}_4)_2\text{N} - \text{C}_6\text{H}_3(\text{CH}_3\text{CONH}) - \text{N} = \text{C}_{10}\text{H}_6\text{O} \\   \\ \text{Ni} \end{array} \right]_2^{2+} \left[ \begin{array}{c} \text{Ar} \\   \\ \text{Ar}-\text{B}-\text{R} \\   \\ \text{Ar} \end{array} \right]_2^-$	phenyl anisyl phenyl	n-butyl n-hexyl n-octyl
30	$\left[ \begin{array}{c} (\text{HOC}_2\text{H}_4)_2\text{N} - \text{C}_6\text{H}_3(\text{CH}_3\text{O}) - \text{N} = \text{C}_{10}\text{H}_6\text{O} \\   \\ \text{Ni} \end{array} \right]_2^{2+} \left[ \begin{array}{c} \text{Ph} \\   \\ \text{Ph}-\text{B}-\text{Bu} \\   \\ \text{Ph} \end{array} \right]_2^-$		

(E)

		Ar	R
31A 31B 31C	$\left[ \begin{array}{c} \text{CH}_3 \\   \\ (\text{CH}_3\text{OOCCH}_2\text{H}_4)_2\text{N}-\text{C}_6\text{H}_4-\text{N}=\text{C}_8\text{H}_6\text{N}-\text{O} \end{array} \right]_2 \text{Ni}^{2+} \left[ \begin{array}{c} \text{Ar} \\   \\ \text{Ar}-\text{B}-\text{R} \\   \\ \text{Ar} \end{array} \right]_2^-$	phenyl anisyl phenyl	n-butyl n-hexyl n-octyl
32	$\left[ \begin{array}{c} \text{C}_4\text{H}_9 \\   \\ (\text{C}_4\text{H}_9)_2\text{N}-\text{C}_6\text{H}_4-\text{N}=\text{C}_8\text{H}_6\text{N}-\text{O} \end{array} \right]_2 \text{Ni}^{2+} \left[ \begin{array}{c} \text{Ph} \\   \\ \text{Ph}-\text{B}-\text{Bu} \\   \\ \text{Ph} \end{array} \right]_2^-$		
33	$\left[ \begin{array}{c} \text{CH}_3 \\   \\ (\text{CH}_3\text{CH}_2)_2\text{N}-\text{C}_6\text{H}_4-\text{N}=\text{C}_8\text{H}_6\text{N}-\text{O} \end{array} \right]_2 \text{Ni}^{2+} \left[ \begin{array}{c} \text{Ph} \\   \\ \text{Ph}-\text{B}-\text{Bu} \\   \\ \text{Ph} \end{array} \right]_2^-$		
34	$\left[ \begin{array}{c} \text{CH}_3 \\   \\ (\text{CH}_3\text{CH}_2)_2\text{N}-\text{C}_6\text{H}_4-\text{N}=\text{C}_8\text{H}_6\text{N}-\text{O} \end{array} \right]_2 \text{Cu}^{2+} \left[ \begin{array}{c} \text{Ph} \\   \\ \text{Ph}-\text{B}-\text{Bu} \\   \\ \text{Ph} \end{array} \right]_2^-$		

(F)

		Ar	R
35	$\left[ \begin{array}{c} (\text{CH}_3\text{CH}_2)_2\text{N}-\text{C}_6\text{H}_4-\text{N}=\text{C}_8\text{H}_6\text{N}-\text{O} \\   \\ \text{CH}_3 \end{array} \right]_2 \text{Ni}^{2+} \left[ \begin{array}{c} \text{Ph} \\   \\ \text{Ph}-\text{B}-\text{Bu} \\   \\ \text{Ph} \end{array} \right]_2^-$		
36	$\left[ \begin{array}{c} (\text{CH}_3\text{CH}_2)_2\text{N}-\text{C}_6\text{H}_4-\text{N}=\text{C}_8\text{H}_6\text{N}-\text{O} \\   \\ \text{CH}_3 \end{array} \right]_2 \text{Ni}^{2+} \left[ \begin{array}{c} \text{Ar} \\   \\ \text{Ar}-\text{B}-\text{R} \\   \\ \text{Ar} \end{array} \right]_2^-$	phenyl anisyl phenyl	n-butyl n-hexyl n-octyl

		Ar	R
37	$\left[ \begin{array}{c} (\text{CH}_3\text{CH}_2)_2\text{N}-\text{C}_6\text{H}_4-\text{N}=\text{C}_6\text{H}_4=\text{O} \\ \text{N} \end{array} \right]_2 \text{Ni}^{2+} \left[ \begin{array}{c} \text{Bu} \\   \\ \text{Bu}-\text{B}-\text{SiPhMe}_2 \\   \\ \text{Bu} \end{array} \right]_2^-$		
38	$\left[ \begin{array}{c} (\text{CH}_3\text{OCC}_2\text{H}_4)_2\text{N}-\text{C}_6\text{H}_3(\text{Cl})-\text{N}=\text{C}_6\text{H}_4=\text{O} \\ \text{N} \end{array} \right]_2 \text{Ni}^{2+} \left[ \begin{array}{c} \text{Ph} \\   \\ \text{Bu}-\text{B}-\text{SiPhMe}_3 \\   \\ \text{Ph} \end{array} \right]_2^-$		

Using an infrared sensitive dye borate in at least one set of the microcapsules enable the sensitivities of the microcapsules to be spaced apart to minimize overlap in their sensitivity curves and thereby minimize crosstalk. Infrared sensitive borates can be used in any or all of the cyan, magenta or yellow forming microcapsules. In one example, an imaging system can be designed in which the microcapsules are sensitive at 750, 850 and 1050 nm. In another embodiment, the red sensitive capsules described in U.S. Patent 4,772,530 (Gottschalk) are replaced with infrared sensitive microcapsules prepared using one of the dyes in the appendix such as the dye #5 in Table 1. In another embodiment an imaging system can be designed in which the microcapsules are sensitive at 800, 900 and 1100 nm. In conventional systems, the cyan, magenta and yellow forming microcapsules are sensitive at 450, 550, 650 nm respectively. In other embodiments of the invention, any of 450, 550, and 650 sensitizers is replaced with an infrared dye. Preferably the magenta 550 initiator is replaced with an infrared dye to achieve the most separation in the absorptions. For example, a 450, 840, 650 nm system might be used.

The infrared sensitive compositions can be modified to include an autoxidizer such as N,N-dimethylaniline as described in U.S. Patent 4,772,530 which is incorporated herein by reference. Likewise, microcapsules for encapsulating the photohardenable composition, cyan, magenta and yellow color precursors, developer materials, photohardenable compositions including photopolymerizable acrylate

compositions are described in detail in U.S. Patent 4,772,530. If it is desired to use an ultraviolet initiator in one or more sets of microcapsules, the ultraviolet initiator can be selected from among those that are known in the art. Some examples are provided in U.S. Patent 4,399,209.

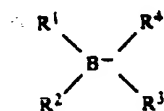
The infrared sensitive dye is normally used in an amount up to 1% by weight based on the weight of the photopolymerizable species and more typically in an amount of about 0.2 to 0.5% by weight. However, those skilled in the art will recognize that the amount is easily adjusted to achieve the desired sensitivity and photographic response in the photosensitive material.

Having described the invention in detail and by reference to preferred embodiments thereof, it will be apparent that modifications and variations are possible without departing from the scope of the invention defined in the appended claims.

What is claimed is:

1. A photosensitive material comprising a support having a layer of microcapsules on one surface thereof, said microcapsules having an image-forming agent associated therewith and containing an internal phase including a photohardenable composition, said composition comprising a free radical addition polymerizable or crosslinkable compound and complex of an infrared sensitive cationic dye and a boranyl anion being capable of absorbing infrared radiation and producing free radicals which initiate free radical polymerization or crosslinking of said polymerizable or crosslinkable compound.

2. The photosensitive material of claim 1 wherein said boranyl anion is represented by the formula I:



where  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ , and  $\text{R}^4$  are independently selected from the group consisting of alkyl, aryl, alkaryl, allyl, aralkyl, alkenyl, alkynyl, alicyclic and saturated or unsaturated heterocyclic groups.

3. The photosensitive material of claim 2 wherein said material is useful in forming full color images and said microcapsules include a first set of microcapsules having a cyan image-forming agent associated therewith, a second set of microcapsules having a magenta image-forming agent associated therewith and a third set of microcapsules having a yellow image-forming agent associated therewith, at least one of said first, second and third sets of microcapsules containing said photohardenable composition contain said complex.

4. The photosensitive material of claim 3 wherein said material is useful in forming images by a process which comprises the steps of image-wise exposing said microcapsules to three distinct wavelengths of actinic radiation which respectively harden said first, second and third sets of microcapsules and subjecting said microcapsules to a uniform rupturing force.



5. The photosensitive material of claim 4 wherein at least one of said wavelengths is greater than 800 nm.
6. The photosensitive material of claim 5 wherein at least one of said sets of microcapsules, other than said set containing said complex, contains a visible light sensitive complex of a cationic dye and a boranyl anion.
7. The photosensitive material of claim 5 wherein at least one of said sets of microcapsules, other than said set containing said complex, contains an ultraviolet sensitive photoinitiator.
8. The photosensitive material of claim 1 wherein the complex is a complex of a dye selected from the dyes in Table 1 or Table 2.
9. The photosensitive material of claim 3 wherein one set of microcapsules is sensitive at about 800 nm, another set is sensitive at about 900 nm and a third set is sensitive at about 1100 nm.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/04131

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 G03F7/029 G03F7/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 223 587 A (THE MEAD CORPORATION) 27 May 1987 cited in the application see page 8; compound 12 see page 13 - page 14; examples 1,2 ----	1-8
X	EP 0 408 227 A (THE MEAD CORPORATION) 16 January 1991 see page 11; compound 13 see claims 1,5,9,15,22 ----	1-8
A	EP 0 438 123 A (SHOWA DENKO KABUSHIKI KAISHA) 24 July 1991 see page 4 - page 8; table 1 see page 10, line 1 ----- -/--	1-9

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

16 June 1999

Date of mailing of the international search report

28/06/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Dupart, J.-M.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/04131

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>           DATABASE WPI            Section Ch, Week 9244            Derwent Publications Ltd., London, GB;            Class A60, AN 92-360898            XP002106181            &amp; JP 04 261405 A (SHOWA DENKO KK)            , 17 September 1992            cited in the application            see abstract         </p>	1-9

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/04131

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0223587 A	27-05-1987	US 4772541 A	20-09-1988
		BR 8605710 A	18-08-1987
		CA 1284740 A	11-06-1991
		DE 3650107 D	24-11-1994
		DE 3650107 T	24-05-1995
		DK 553786 A	21-05-1987
		EP 0389067 A	26-09-1990
		JP 2726258 B	11-03-1998
		JP 62143044 A	26-06-1987
		JP 2711447 B	10-02-1998
		JP 62150242 A	04-07-1987
		KR 9402538 B	25-03-1994
		US 4977511 A	11-12-1990
		US 4842980 A	27-06-1989
		US 4865942 A	12-09-1989
		US 4937159 A	26-06-1990
		US 5151520 A	29-09-1992
		US 5035621 A	30-07-1988
		US 4895880 A	23-01-1990
		US 4772530 A	20-09-1988
		US 4800149 A	24-01-1989
EP 0408227 A	16-01-1991	JP 3163106 A	15-07-1991
EP 0438123 A	24-07-1991	DE 69112852 D	19-10-1995
		DE 69112852 T	15-05-1996
		JP 5194619 A	03-08-1993